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The Raman Spectrum of α -Zirconium Fluoride and Implications for the Bridging Modes of Fluorozirconate Glass

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The previously undetermined Raman spectrum of α -ZrF₄ is reported and used to interpret the Raman spectra of binary barium fluorozirconate glasses. Under the assumption of separability of the motions of different types of bridging fluoride ions, it is shown that the "edge," or doubly bridging, fluoride structure exhibits a characteristic band in the α -ZrF₄ crystal spectrum which is also identifiable in the glass spectra, in contrast to previous interpretations. New assignments are proposed for the main peaks in the fluorozirconate glass spectra, and an approximate mathematical treatment is used to explain the observed frequencies of the two types of bridging Zr-F bonds.

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I. INTRODUCTION

Glasses based on ZrF₄ are of interest because of their infrared transparency, their anionic conductivity, and their unusual structures. The promise of fluorozirconate glass as a fiber optic material is based on its ability to transmit farther into the infrared region (the region used for optical telecommunications) than does silica glass and the fact that, properly purified, it theoretically could surpass the transparency of silica.¹ Fluorozirconate glasses are fast ionic conductors at elevated temperatures, so they are prospective solid electrolytes.² In addition to their practical applications, these glasses are of theoretical interest because, with nonpolarizable fluoride ions as the dominant species, they are more ionic than the familiar oxide glasses and appear to possess fundamentally different structures.³ For instance, the existence of common oxide glasses is usually explained by the presence of three-dimensional arrays of low-coordination-number cations connected through highly directed covalent bridge bonds, but the fluorozirconate glasses evidently contain more densely packed groupings with high coulomb energies.

A knowledge of the short-range structure of these glasses is necessary for a greater understanding of their properties, but the present picture of the structure is incomplete. Although X-ray diffraction measurements, vibrational spectroscopic studies, and molecular dynamics simulations have provided structural information, different authors have drawn conflicting conclusions from these methods.⁴⁻¹³ The major points of contention involve the fluorine-about-zirconium coordination number and the nature of the fluoride-ion bridging between zirconium ions. This paper is concerned only with the aspect of bridging.

The first structural study of the binary barium fluorozirconate glasses⁴ was carried out in 1981 by Almeida and Mackenzie, who compared the glass vibrational spectra with the spectra of crystalline alkali metal fluorozirconates. A subsequent paper on the structure of barium

fluorohafnate glass⁵ contained minor revisions and additions to the original results. The authors concluded that, for the prototypical $\text{BaZr}_2\text{F}_{10}$ composition, there were octahedral ZrF_6 units connected together in zigzag chains that were crosslinked by Ba-F ionic bonds. In other words, Almeida and Mackenzie allowed for only one type of bridging, the type in which two Zr ions are connected by a single F ion. This type of bridge will be referred to as "corner-sharing," in reference to the shared vertices of the ZrF_n polyhedra.

Another type of bridge, a double fluoride bridge to be referred to as "edge-sharing," is also seen in fluorozirconate crystals. In fact, all the closest crystalline analogs of the barium fluorozirconate glasses contain some degree of edge-bridging, as does one of the modifications of ZrF_4 . In spite of this, no mention was made of the possibility of edge-sharing in the glass until 1983, when Kawamoto,^{6,7} on the basis of similarities between the glass and crystal Raman spectra, DTA curves, and X-ray data, speculated that BaZrF_6 glass consists of chains of edge-shared ZrF_8 dodecahedra. Later, Lucas et al.⁸ used results from molecular dynamics simulations to interpret earlier data from X-ray studies⁹ as indicative of the existence of a combination of edge-sharing and corner-sharing in the glasses. Subsequent molecular dynamics calculations of fluorozirconate glass by other groups¹⁰⁻¹³ also showed evidence of edge-bridging. In 1985, Almeida et al.¹⁴ stated that their X-ray photoemission results suggested the possible occurrence of edge-bridging in the 55 mol % ZrF_4 -45 mol % BaF_2 glass. Also in 1985, Walrafen et al.¹⁵ studied the Raman spectra of fluorozirconate glasses and melts and tentatively assigned one of the glass peaks to an edge-bridging moiety, but they did not justify the assignment.

It would be very useful if a characteristic region for the occurrence of an edge-bridging band could be identified in the vibrational spectra of fluorozirconate crystals. If so, this information could be used to determine spectroscopically whether or not edge-sharing is present in the fluorozirconate glasses. The two crystalline polymorphs of ZrF_4 whose structures are known represent a particularly simple collection of Zr-F bonding types, in that they both contain only bridging fluorides and 8-coordinate zirconium ions. The β -polymorph exhibits only corner-bridging, and the α -polymorph contains both corner and edge fluorides. Assuming that the corner and edge types of vibration are not strongly coupled, the main difference in the Raman spectra of the two ZrF_4 crystals would be the appearance of an extra peak due to edge-bridging in the α -modification. This expectation was verified. In this paper we present the previously unknown Raman spectrum of the α - ZrF_4 crystal and show how its features provide a clarification of the ~ 325 - 500 cm^{-1} region of the Raman spectra of the fluorozirconate glasses.

II. EXPERIMENTAL PROCEDURE

Crystals of α - and β - ZrF_4 were obtained by sublimation of commercially available 99% ZrF_4 (Cerac). The starting material was placed in a 30-cm-long nickel tube which was sealed with a Swagelok valve fitting and then evacuated. The nickel tube was inserted into a tube furnace which kept the starting material at a temperature of about 900°C and produced a steadily decreasing temperature gradient down the length of the tube. The relatively large, well-formed β -crystals were retrieved from the part of the tube which was kept at temperatures between 450 and 900°C . Thin polycrystalline films of α - ZrF_4 were deposited in the cooler regions, as described by Gaudreau.¹⁶ The identities of the crystals were confirmed by X-ray diffraction

measurements.

Raman spectra were obtained using a Spectra Physics Model 165 Ar⁺ laser, a Spex Industries model 1403 double monochromator, a cooled RCA C31034-02 PMT, and standard photon counting electronics. The excitation geometry was such that the samples were illuminated with a focused (0.5mm) beam of 514.5 nm light at a power of ~150 mW at an angle of 60° from the surface normal. Scattered radiation was collected with an *f*/0.95 camera lens (D. O. Industries) orthogonal to the incident light and focused onto the monochromator's entrance slit using *f*-matching achromatic optics. Spectra were typically recorded using a bandpass of 5 cm⁻¹ determined by the exit slit, 2 second integration time, and a 0.5 cm⁻¹ step size. A flat, opaque, polycrystalline sample of α-ZrF₄ was spun during the Raman experiment. The sample of β-ZrF₄ used was a large, transparent polycrystal. Due to the polycrystalline nature of the samples, it was not possible to obtain polarization information.

III. RESULTS

The spectrum of β-ZrF₄ is shown in Fig. 1a. The results generally agree with previously published data.^{17,18} The main features are located close to 400 cm⁻¹. There are two medium peaks at 384 and 417 cm⁻¹ (the 417 cm⁻¹ band is broad) and two weaker peaks at 357 and 478 cm⁻¹. Goldstein et al.¹⁷ found a medium peak at 391 cm⁻¹ and medium-to-medium-strong peaks at 407 and 425 cm⁻¹, as well as weak peaks at 345 and 484 cm⁻¹. The appearance of the Fig. 1a spectrum is also in accord with the ZrF₄ spectrum of Kawamoto.¹⁸ The polymorph studied by Kawamoto was later identified as the β-variety.¹⁹

Fig. 1b shows the Raman spectrum of α-ZrF₄. In analogy with the β-ZrF₄ spectrum, there are medium peaks at 351, 397, and 416 cm⁻¹. The most prominent difference from the β-spectrum is the presence of a sharp, medium-strong peak centered at 512 cm⁻¹. It is possible that Goldstein et al.¹⁷ recorded a peak of similar origin in their study of the isomorphic compound HfF₄. They stated that the X-ray diffraction pattern of their HfF₄ sample showed contamination from an unidentified polymorph, and their HfF₄ Raman data include a strong peak at 500 cm⁻¹.

IV. DISCUSSION

In this section, we will first review previous observations and assignments and then discuss possible conceptual problems before applying the information contained in the differences between the α- and β-ZrF₄ spectra to the interpretation of fluorozirconate glass structure.

A. Previous Vibrational Assignments in the Glass

The Raman spectra of some barium fluorozirconate glasses as determined by Almeida and Mackenzie⁴ are reproduced in Fig. 2. These spectra exhibit three main Raman peaks in the Zr-F stretching region (frequencies greater than 400 cm⁻¹)²⁰ of the glasses:

- 1) a polarized peak between 565-598 cm⁻¹,
- 2) a less-strongly polarized peak at 468-500 cm⁻¹, and

- 3) a weaker, depolarized band at $386\text{-}416\text{ cm}^{-1}$. (Walrafen et al.¹⁵ described this peak as being weakly polarized, and Almeida and Mackenzie found a partially polarized band for HfF_4 .⁵)

The bands in the bending region were weakly polarized (in the case of HfF_4)⁵ and occurred at the following positions:

- 4) $322\text{-}348\text{ cm}^{-1}$ and
- 5) $183\text{-}196\text{ cm}^{-1}$.

The first peak mentioned above is the dominant feature of the fluorozirconate glass spectra. There is little doubt that this strong, sharp, polarized peak is due to the symmetric "breathing" stretch of the terminal (nonbridging) fluorides. It does not appear in the Raman spectra of HfF_4 and $\beta\text{-ZrF}_4$,^{17,18} two crystals which contain only bridging fluorides, but it is present in the spectra of all fluorozirconate crystals, which necessarily contain some fluoride ions that do not bond only to zirconium.

The other two peaks in the stretching region have not been assigned with certainty. Walrafen et al.¹⁵ observed a decrease in band intensity in the $\sim 325\text{-}500\text{ cm}^{-1}$ region upon melting. They concluded from this that the bands between ~ 325 and 500 cm^{-1} were due to corner- and edge-bridging vibrations, but they did not suggest a way to distinguish between the two contributions. Almeida and Mackenzie at first attributed Peak 2 to a symmetric stretch of the corner (singly bridging) fluorides⁴ and later reassigned it, in spite of its polarized nature and its relatively important intensity, as an antisymmetric stretch which was IR active but weakly allowed in Raman.⁵ In their reassignment, they attributed the $183\text{-}196\text{ cm}^{-1}$ peak (Peak 5) to the symmetric stretch of the bridging fluorides plus cation motion. This would mean that the symmetric and antisymmetric stretching modes are separated by about 300 cm^{-1} , which would be highly unusual. For instance, the symmetric (A_g) and antisymmetric (B_g) stretching modes of the bridging atoms in ZrCl_4 are separated by 26 cm^{-1} , those in ZrBr_4 by 40 cm^{-1} .²¹ As noted in the Introduction, Walrafen et al.¹⁵ tentatively assigned Peak 2 to a doubly bridging fluoride stretch, but they offered no justification.

The third peak was first assigned by Almeida and Mackenzie to an antisymmetric stretch of the terminal fluorides in free ZrF_4^{2-} ions⁴ and was later tentatively reassigned as an antisymmetric stretch of the terminal fluorides in the chain.⁵ Since, as discussed above, the major contribution to this region seems to be due to bridging fluorides, any effect from terminal stretches would probably be negligible. Walrafen et al.¹⁵ surmised that Peak 3 was due to edge-sharing between the Pb ions in their sample, but the peak appears in lead-free glasses as well. Moreover, the frequency of this proposed edge-sharing would be expected to be much lower than the Zr-F bridging frequency since it would involve Pb(II)-F bonds rather than Zr(IV)-F bonds. Almeida and Mackenzie⁵ tentatively assigned Peak 4 to terminal bending modes, and, as mentioned above, Peak 5 was assigned to a symmetric stretch of the bridging fluorides with some Zr motion.

B. Relating Crystal Spectra to Glass Spectra

Since the structures occurring in fluorozirconate glasses are not known with certainty, there is necessarily some doubt associated with any interpretation of the glass spectral features. The

structures of certain fluorozirconate crystals are known with certainty, and the question of whether crystal spectra can be used as standards of reference for the glasses naturally arises. The interpretation of glass spectra by comparison with the spectra of related crystals presupposes that any structural similarities between the two will be reflected in bands of similar frequency and, in some cases, similar appearance. If separability of bands (see Section IV.C.) is assumed, there is no apparent reason to reject this supposition. Of course, the utility of the method depends on the correct interpretation of the crystal spectra.

There is ample precedent for the judicious use of the "fingerprint" approach to gain insight into glass structure by comparing glass spectra with the spectra of related crystals.²²⁻²⁴ This has been done previously for the vibrational spectra of the fluorozirconate glasses.^{4-6,18} In addition, comparisons between glass and crystal data have been used to interpret X-ray diffraction data,^{7,9,25} X-ray photoemission spectroscopy¹⁴, and visible spectroscopy²⁶ of fluorozirconate glasses.

C. Separability of Fluoride-Ion Motions

In order to assign the observed Raman peaks to motions of terminal, edge, or corner fluoride ions, it must be assumed that the motions are separable. In other words, a normal mode responsible for a peak must involve the movements of predominantly one type of fluoride. This is often true in the case of vibrations involving light atoms which are separated by a heavy central atom such as zirconium. Consider the bonding situation X-Zr-Y, where X and Y are two different substituents whose masses are small in comparison to the Zr mass. In this case, a large vibrational amplitude of Zr-Y will result in only a small distortion of X-Zr; the Zr acts as a buffer between the vibrations of the attached ligands. (See Ref. 27.)

It has been demonstrated already that the terminal fluoride stretching motion is separable, to a very good approximation, from the bridging motion: the vibrational mode responsible for Peak 1 is almost completely suppressed in the absence of terminal fluorides. In the case of simple Al_2Cl_6 dimers in the liquid state, the terminal and bridge frequencies are clearly separated.²⁸ For the more complex crystalline solids ZrCl_4 and ZrBr_4 , which contain only terminal and edge fluorides, a normal-mode analysis²¹ has shown that the contribution of the terminal bond stretch to the high-frequency A_g mode is 96% for ZrCl_4 and 86% even for ZrBr_4 , which contains relatively heavy halogen atoms.

The requirement for the separability of the bridging peaks (Peaks 2 and 3) is that the singly bridging fluoride bonds are sufficiently different from the bonds involving doubly bridging fluorides. If so, then they may be treated as two different types of ligands on a zirconium atom, as discussed above. As shown by X-ray studies of fluorozirconate crystals, the corner- and edge-bridging Zr-F bonds are distinguishable by their lengths and by their Zr-F-Zr angles. (See Appendix.) In addition, an edge fluoride is constrained to a smaller range of angles because of the proximity of its bridging neighbor. So it is possible that the edge and corner vibrations are sufficiently decoupled to give rise to separate, characteristic peaks.

With the assumption of separability, the differences in the spectra of $\alpha\text{-ZrF}_4$ and $\beta\text{-ZrF}_4$ should give valuable information about the positions of edge- and corner-sharing peaks. Both crystals contain 8-coordinate Zr, but the β -modification contains only corner-shared fluoride

ions,²⁹ while the α -modification contains 75% corner-shared and 25% edge-shared fluorides.³⁰ Thus, it would be expected that the major differences between the two spectra, in particular the appearance of any extra peaks in the α -spectrum, would be due to the presence of the edge-sharing structure.

D. New Assignments for Fluorozirconate Glass Peaks

In view of the above considerations, it seems highly plausible that the relatively sharp 512 cm^{-1} band of Fig. 1b (shown in the Results Section to be the major difference between the Zr-F stretching regions of the α - and β -ZrF₄ spectra) is the signature of the Zr(F₂)Zr edge-sharing structural motif in the crystal. This basis will be used for a reassignment of the fluorozirconate Raman bands. This Section section is largely devoted to the interpretation of Peaks 2 and 3 (see Fig. 2), since there is no reason to question the assignment of Peak 1 as the symmetric terminal stretch.

By comparison with the 512 cm^{-1} edge-bridging stretch in the crystal, Peak 2 (typically occurring at about 490 cm^{-1}) of the fluorozirconate glasses can be assigned to the stretching modes of doubly bridging fluorides and probably includes both symmetric and antisymmetric contributions, since the analogous peaks are so close together in ZrCl₄ and ZrBr₄. (See Section IV.A.) This is also the case for Al₂Cl₆, in which the ν_2 (A_{1g}) and ν_6 (B_{1g}) edge peaks occur at 339 and 330 cm^{-1} , respectively.²⁸

The higher frequency of the α -ZrF₄ edge peak as compared to the edge peak of the fluorozirconate glasses is probably due to the greater degree of bridging in the crystal. In other words, the substitution of short, strong terminal bonds for some of the bridging bonds (which is what happens as ZrF₄ changes to a fluorozirconate) reduces the electron density available to the remaining bridging bonds and causes their vibration frequencies to decrease. Indeed, the peaks attributable to edge-bridging in the alkaline earth fluorozirconate crystals α -BaZrF₆, β -BaZrF₆, and α -SrZrF₆ all occur at frequencies less than 500 cm^{-1} .⁶

Peak 3 of the glass, in comparison with the band observed for β -ZrF₄, encompasses contributions from the corner-sharing fluorides. This peak is broader than Peak 2, a condition which would be expected in light of the broader range of angles available to the singly bridging fluorides. Unfortunately, there could be some confusion in this area of the spectrum (around 400 cm^{-1}) because of other bands occurring nearby at lower frequencies. For example, the fluorozirconate crystals of Ref. 6 exhibit bands in the 350-400 cm^{-1} region even though they do not contain corner bridges. These bands could be due to movements of edge fluorides or to bending motions of the terminal fluorides.

Since Peak 4 is near a region which lost no intensity upon melting,¹⁵ it is probably due to some type of terminal deformation, in agreement with the assignment of Almeida and Mackenzie⁵ and the corresponding assignments²¹ for ZrCl₄ and ZrBr₄. Peak 5, which did lose intensity upon melting,¹⁵ could be at least partially due to a symmetric ring deformation involving the edge-sharing structure, as is seen for ZrCl₄ and ZrBr₄.²¹ A normal-mode analysis²⁸ showed that the corresponding ring deformation for Al₂Cl₆ (ν_4 , A_{1g} symmetry) involves the simultaneous inward motion of the edge fluorides and outward motion of the cations. In support of this assignment for Peak 5, which is usually located at frequencies slightly

below 200 cm^{-1} , there is a prominent peak at 206 cm^{-1} in the $\alpha\text{-ZrF}_4$ spectrum. In addition, Goldstein et al.¹⁷ report a strong peak at 205 cm^{-1} in the Raman spectrum of their mixed-polymorph HfF_4 sample which is not present in their ZrF_4 spectrum. Walrafen et al.¹⁵ also speculated that the $100\text{-}300\text{ cm}^{-1}$ region contains contributions from edge-sharing moieties.

The present assignments are summarized in Table I for the case of the prototypical barium dizirconate glass. The frequencies shown were determined by Almeida and Mackenzie.⁴

V. CONCLUSION

Other than the pioneering studies by Almeida and Mackenzie,^{4,5} there have been few attempts¹⁵ to make specific assignments to the peaks observed in the Raman spectra of barium fluorozirconate glasses. In this paper the previously undetermined Raman spectrum of $\alpha\text{-ZrF}_4$ yielded the location of the frequency range of the edge-sharing band. Since a peak was found in the same area of the glass spectra, this information, although indirect, represents the first spectral evidence for edge-sharing in the glass. The second- and third-highest-frequency bands of the glass Raman spectra were reassigned according to this interpretation.

One of the goals of this study was a clarification of the extent to which vibrational spectroscopy can be used as a "fingerprinting" technique in the study of amorphous solids. Based on comparisons with ZrCl_4 and ZrBr_4 spectra, it seems plausible that, at least in fluorozirconate glasses, the motions of the different types of fluoride ions are sufficiently decoupled to produce separate peaks in identifiable regions of the spectrum, thereby allowing the use of the spectra of related crystals as diagnostic tools.

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Mathematical Treatment of Bridging Modes

The proposed assignment of the second peak to edge-bridging and the third to corner-bridging may seem anomalous at first, since the second peak is of higher frequency than the third and edge Zr-F bonds are longer than corner bonds. However, for bridging fluorides the effect of the Zr-F-Zr angle must be taken into account. This may be done using a very simple (and approximate) formula from Ref. 4:

$$\omega = \frac{1}{2\pi c} \sqrt{\frac{2k \cos \frac{\theta}{2}}{m_F}}, \quad (1)$$

where ω is the observed frequency in wavenumbers, c is the speed of light in cm/s, k is the force constant of a bridging Zr-F bond in dynes/cm, θ is the Zr-F-Zr angle in degrees, and m_F is the mass in grams of a fluorine atom. This equation assumes no movement of Zr ions. The form of the equation for the symmetric stretch of a nonbridging (terminal) fluoride is, of course,

$$\omega = \frac{1}{2\pi c} \sqrt{\frac{k}{m_F}}. \quad (2)$$

The terminal stretch frequencies ranging between 565 and 598 cm^{-1} for the glasses⁴ yield values of 3.58-4.01 mdyne/ \AA for the force constant of a terminal Zr-F bond. Brown et al.³¹ state that the stretching force constant of a bond is proportional to the bond strength. Therefore, the formula

$$k_B = \frac{s_B}{s_T} \cdot k_T, \quad (3)$$

where B refers to a bridging fluoride (corner or edge) and T is a terminal fluoride, allows the calculation of bridging force constants from the already calculated terminal force constant. The empirically determined formula

$$s = e^{(1.846 - r)0.37}, \quad (4)$$

which is due to Brown and Altermatt,³² gives the strength of a Zr-F bond of length r , where r is in \AA units. Since for the barium fluorozirconate crystals of known structure⁽³⁴⁻³⁶⁾ the s_C/s_T ratio is 0.763 and the average s_E/s_T ratio is 0.604, the range of values for k_C is 2.73-3.06 mdynes/ \AA , and for k_E it is 2.16-2.42 mdynes/ \AA . The values of θ_C and θ_E for barium fluorozirconate crystals are 143° and 115° , respectively. Substituting these quantities into Eq. 1 yields calculated values of 455-482 cm^{-1} for ω_E and 393-416 cm^{-1} for ω_C . These results, although only crude approximations, agree surprisingly well with the observed frequencies of 468-500 cm^{-1} and 386-416 cm^{-1} .⁴

The stretching force constant for bridging Zr-F bonds has been reported to be 1.32 mdynes/ \AA .³³ This value is less than half the stretching force constant for the terminal Zr-F bonds. If accurate, this value represents an unusual situation, since the bond order for a fluoride shared between two Zr ions would be expected to be about half that of a terminal fluoride, or greater than half if the interaction between countercations and bridging fluorides is weaker than the countercation-terminal fluoride interaction. In contrast to this result, the approximate

bridging force constants calculated above (between 2 and 3 mdynes/Å) are over half the magnitude of the terminal force constant (between 3 and 4 mdynes/Å).

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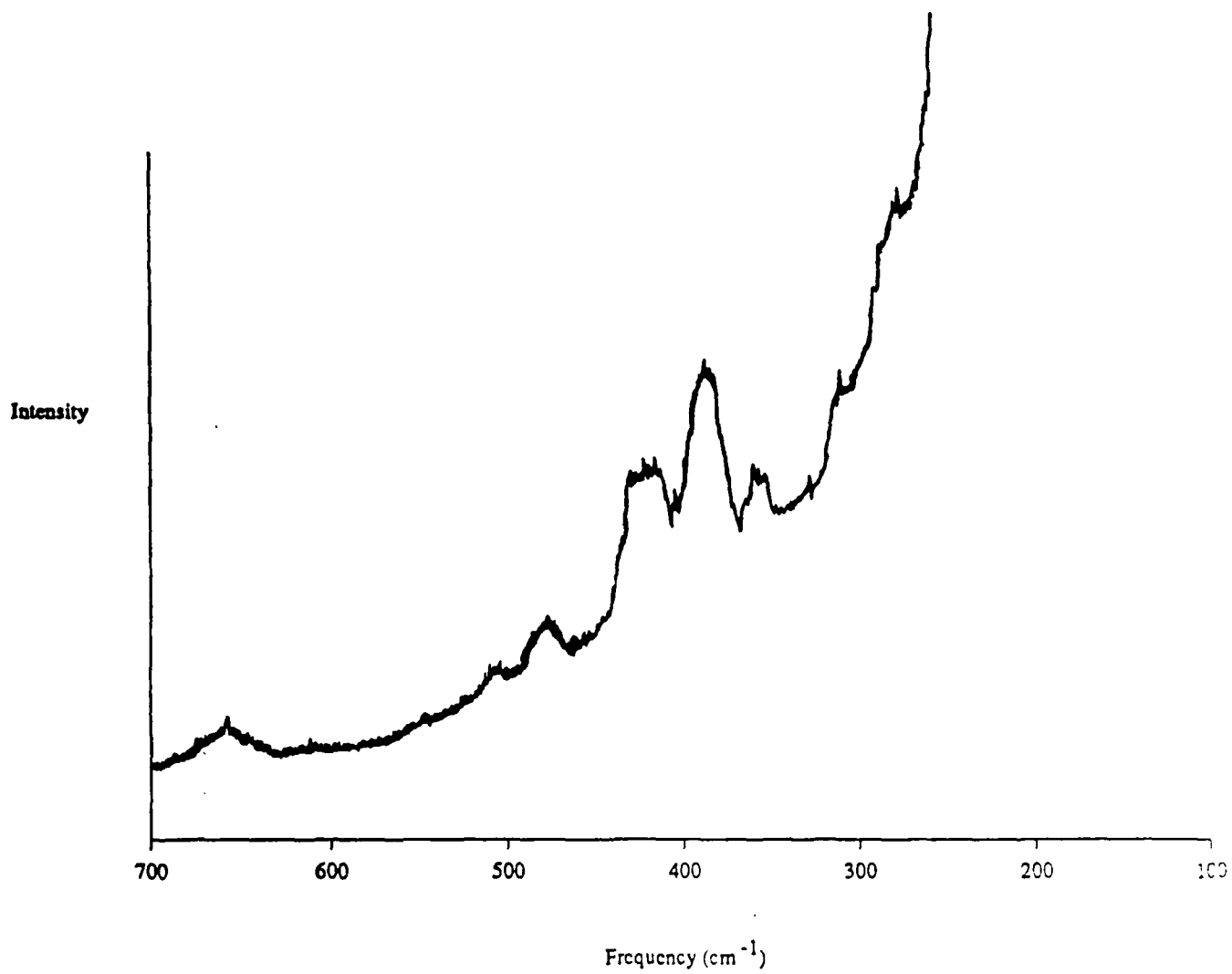
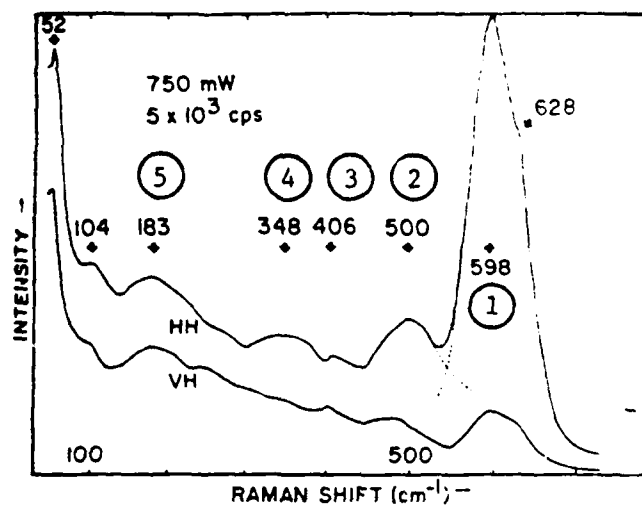
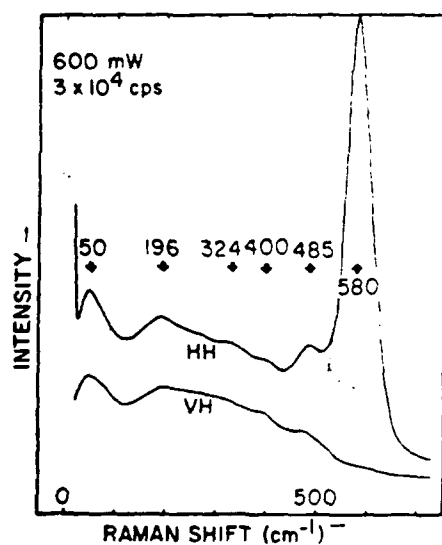


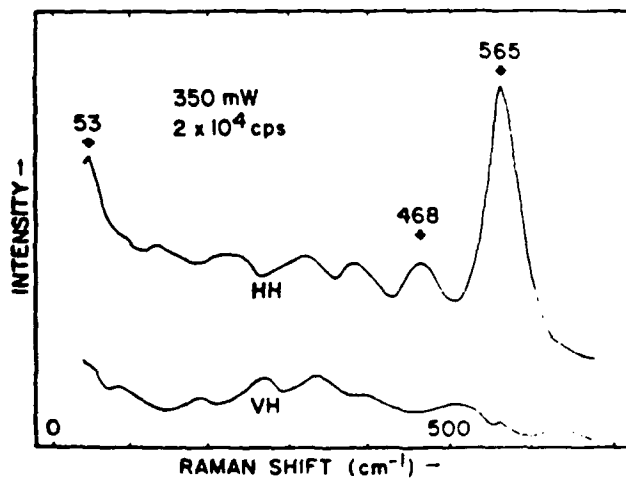
Figure 1a. The Raman spectrum of β -ZrF₄.



74 mol % ZrF₄



64 mol % ZrF₄



52 mol % ZrF₄

Figure 2. Raman spectra of some barium fluorozirconate glasses (from Ref. 4). The Peak numbers used in the text are shown for the 74 mol % ZrF₄ composition.